

# Origin of $T_c$ Enhancement Induced by Doping Yttrium and Hydrogen into LaFeAsO-based Superconductors: $^{57}\text{Fe}$ -, $^{75}\text{As}$ -, $^{139}\text{La}$ -, and $^1\text{H}$ -NMR Studies

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We report our extensive  $^{57}\text{Fe}$ -,  $^{75}\text{As}$ -,  $^{139}\text{La}$ -, and  $^1\text{H}$ -NMR studies of  $\text{La}_{0.8}\text{Y}_{0.2}\text{FeAsO}_{1-y}$  ( $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$ ) and  $\text{LaFeAsO}_{1-y}\text{H}_x$  ( $\text{La1111H}$ ), where doping yttrium (Y) and hydrogen (H) into optimally doped  $\text{LaFeAsO}_{1-y}$  ( $\text{La1111(OPT)}$ ) increases  $T_c=28$  K to 34 and 32 K, respectively. In the superconducting (SC) state, the measurements of nuclear-spin lattice-relaxation rate  $1/T_1$  have revealed in terms of a multiple fully gapped  $s_{\pm}$ -wave model that the SC gap and  $T_c$  in  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  become larger than those in  $\text{La1111(OPT)}$  without any change in doping level. In  $\text{La1111H}$ , the SC gap and  $T_c$  also increase slightly even though a decrease in carrier density and some disorders are significantly introduced. As a consequence, we suggest that the optimization of both the structural parameters and the carrier doping level to fill up the bands is crucial for increasing  $T_c$  among these  $\text{La1111}$ -based compounds through the optimization of the Fermi surface topology.

KEYWORDS: superconductivity, iron-based oxypnictide,  $\text{LaFeAsO}$ , NMR

Immediately after the discovery of superconductivity (SC) in the iron-oxypnictide  $\text{LaFeAsO}_{1-x}\text{F}_x$  ( $T_c = 26$  K),<sup>1</sup> it was reported that the replacement of La by other rare-earth ( $Ln$ ) elements significantly increases the transition temperature  $T_c$  up to more than 50 K.<sup>2–4</sup> Lee *et al.* found that  $T_c$  increases up to a maximum of 55 K when the  $\text{FeAs}_4$  tetrahedron is transformed into a regular one.<sup>5</sup> Related to this, structural parameters such as the  $a$ -axis length<sup>4,6,7</sup> and height of pnictogen from the Fe plane<sup>8</sup> also exhibit an intimate correlation with  $T_c$  in the  $Ln\text{FeAsO}(Ln1111)$  system. Systematic measurements by spectroscopies have been performed extensively on  $M\text{Fe}_2\text{As}_2(M122)$  and  $\text{FeSe}$  systems, probing the multiband character of their Fermi surfaces and the development of antiferromagnetic (AFM) spin fluctuations, but not sufficiently on  $Ln1111$  systems because high-quality single crystals of sufficiently large size are not yet available.<sup>9</sup> In previous NMR studies of  $\text{Nd1111}$  ( $T_c=53$  K) and  $\text{Pr1111}$  ( $T_c=47$  K),<sup>10,11</sup>  $4f$ -electron-derived magnetic fluctuations prevented us from deducing the normal-state properties and SC characteristics of  $\text{FeAs}$  layers. Under these situations, the reason why  $T_c$  is highest in the  $Ln1111$  system has not yet been addressed. Recently, it has been reported that  $T_c$  can be increased by either Y or H substitution in the  $\text{La1111}$  system without replacing magnetic rare-earth elements,<sup>6,12,13</sup> in which the angle  $\alpha$  of As-Fe-As bonding and the  $a$ -axis length approach those of the  $\text{Nd1111}$  system with the highest  $T_c$  to date (see Fig. 1(a)).

In this Letter, we report the normal-state and SC characteristics of  $\text{La}_{0.8}\text{Y}_{0.2}\text{FeAsO}_{1-y}$  ( $T_c = 34$  K) and  $\text{LaFeAsO}_{1-y}\text{H}_x$  ( $T_c = 32$  K) determined using extensive NMR measurements of  $^{57}\text{Fe}$ -,  $^{75}\text{As}$ -,  $^{139}\text{La}$ -, and  $^1\text{H}$ . We address the important correlation between the evolution

of the electronic state caused by Y and H substitutions and the optimization of the local structure of the  $\text{FeAs}_4$  tetrahedron in these  $\text{La1111}$  systems.

$^{57}\text{Fe}$ -enriched polycrystalline samples of  $\text{La}_{0.8}\text{Y}_{0.2}\text{FeAsO}_{0.7}$  and  $\text{LaFeAsO}_{0.58}\text{H}_{0.58}$  each with a nominal composition were synthesized via a high-pressure synthesis technique.<sup>3,6,13</sup> Although the oxygen and hydrogen contents of the samples differ from the nominal composition during the oxidation of the starting rare-earth elements, the X-ray diffraction measurements indicate that these samples are almost of a single phase. We hereafter denote these samples as  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$ . The respective  $T_c=34$  and 32 K for  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$  were uniquely determined by a steep variation in susceptibility, being higher than  $T_c=28$  K for  $\text{La1111(OPT)}$ .<sup>14,15</sup> As shown in Fig. 1(a), which was reported in the literature,<sup>4,6,7</sup> note that the  $a$ -axis length of  $\text{La1111H}$  and  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  is closer to the optimum value for reaching the maximum  $T_c$  than that of optimally doped  $\text{LaFeAsO}_{1-y}$  ( $\text{La1111(OPT)}$ ). The NMR measurements of  $^{57}\text{Fe}$ -,  $^{75}\text{As}$ -,  $^{139}\text{La}$ -, and  $^1\text{H}$  were performed on most oriented powder samples of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$ . The nuclear spin-lattice relaxation rate ( $1/T_1$ ) was measured in the field  $H \perp c$  by the saturation-recovery method.

Figure 1(b) shows the  $^{57}\text{Fe}$ -NMR spectra obtained by sweeping a frequency ( $f$ ) at a magnetic field  $H = 11.97$  T at 30 K. The  $^{57}\text{Fe}$ -NMR spectra become broader in  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$  than in  $\text{La1111(OPT)}$ <sup>15</sup> as a result of the substitution of either Y or H. In particular, an extremely broadened  $^{57}\text{Fe}$ -NMR spectral width of  $\text{La1111H}$  is almost independent of temperature, suggesting that H doping makes local magnetic states quite inhomogeneous through the distribution of uniform spin susceptibility and/or the hyperfine-coupling constant at

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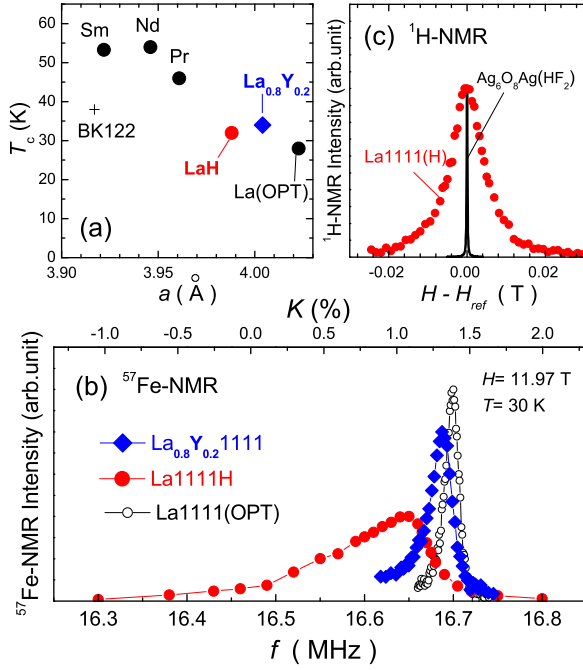


Fig. 1. (color online) (a) Plot of  $T_c$  vs  $a$ -axis length for  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$ ,  $\text{La1111H}$ , and  $\text{Ln1111}$  systems.<sup>6,7</sup> (b) Comparison of the  $^{57}\text{Fe}$ -NMR spectra of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$  at 30 K with that of  $\text{La1111(OPT)}$ .<sup>15</sup> (c) Comparison of the  $^1\text{H}$ -NMR spectrum in  $\text{La1111H}$  with that of stoichiometric compound  $\text{Ag}_6\text{O}_8\text{Ag}(\text{HF}_2)$  at  $H \sim 3.916$  T and  $T \sim 100$  K.

the Fe site. By contrast, the  $^{57}\text{Fe}$ -NMR spectral width of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  is significantly narrower than that of  $\text{La1111H}$ . This suggests that the  $\text{Y}^{3+}$  substitution for  $\text{La}^{3+}$  introduces fewer disorders than H-doping. The  $^1\text{H}$ -NMR spectrum for  $\text{La1111H}$  is presented in Fig. 1(c). Note that the  $^1\text{H}$ -NMR spectral width of approximately 90 Oe is much broader than those of stoichiometric compounds including H ions located at a regular crystallographic site, for instance, 2.6 Oe in  $\text{Ag}_6\text{O}_8\text{Ag}(\text{HF}_2)$ . This may be due to the wide distribution of the transferred hyperfine fields at the H site induced by Fe-spin polarization. Since the  $^1\text{H}$ -NMR spectral shape is symmetric, most of the H ions may occupy a single site within the  $\text{LaFeAsO}$  structure.

In order to shed further light on the local disorder introduced by substitution, we compare the site dependences of the NMR spectral widths ( $W$ ) at 40 K measured by  $^{57}\text{Fe}$ -,  $^{75}\text{As}$ -, and  $^{139}\text{La}$ -NMR in  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$ , as shown in Fig. 2. Here, each  $W$  is normalized by  $W_0$  defined by that of  $\text{La1111(OPT)}$ . In  $\text{La1111H}$  ( $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$ ), the ratio of the linewidth  $W/W_0$  at the Fe and La sites is larger (smaller) than that at the As site, suggesting that the H ions occupy an interstitial site between the La and Fe sites, which induces local disorder especially at Fe and La sites. Taking the decrease in the carrier density of  $\text{La1111H}$  into account, to be discussed later, the doped H ions will exist as negatively charged  $\text{H}^-$  ions, which may be stable at the interstitial site surrounded by positively charged  $\text{La}^{3+}$  and  $\text{Fe}^{2+}$  ions, as indicated in the inset of Fig. 2(a).

Figure 3(a) shows the  $T$  dependences of  $^{75}(1/T_1T)$

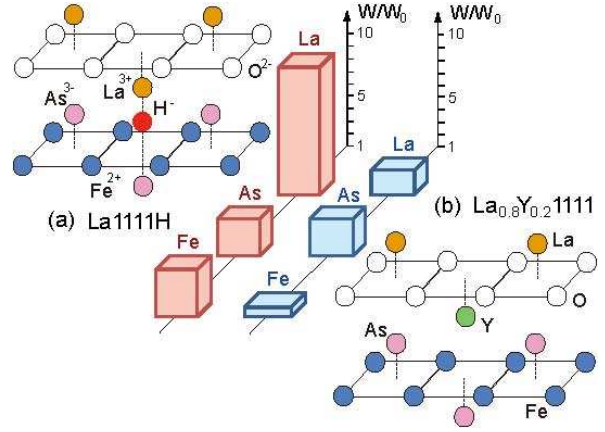


Fig. 2. (color online) Site dependences of the NMR spectral width ( $W$ ) at 40 K of  $^{57}\text{Fe}$ ,  $^{75}\text{As}$ , and  $^{139}\text{La}$  for (a)  $\text{La1111H}$  and (b)  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$ . Each  $W$  is normalized by  $W_0$  defined by those of  $\text{La1111(OPT)}$ . In  $\text{La1111H}$  ( $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$ ), each  $W/W_0$  at the Fe and La sites is larger (smaller) than that at the As site, suggesting that the H ions predominantly occupy an interstitial site between the La and Fe sites. Taking the decrease in the carrier density of  $\text{La1111H}$  into account, the doped H ions will exist as negatively charged  $\text{H}^-$  ions.

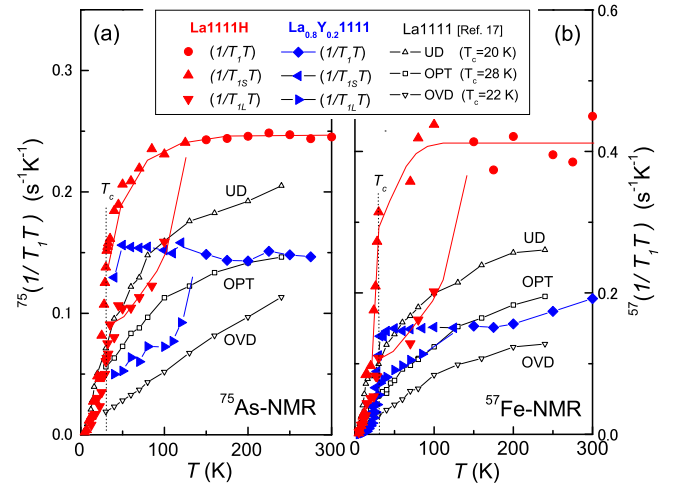


Fig. 3. (color online)  $T$  dependences of  $1/T_1T$ s of (a)  $^{75}\text{As}$ - and (b)  $^{57}\text{Fe}$ -NMR for  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$ . The comparison with those of  $\text{La1111}$  compounds<sup>16</sup> reveals that the electron doping level of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  is close to that of  $\text{La1111(OPT)}$ ,<sup>16,17</sup> but that  $\text{La1111H}$  is in the underdoped regime.

for  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$ . In both compounds,  $^{75}(1/T_1)$  can be determined by a single  $T_1$  component above  $\sim 150$  K, indicating that the electronic state seems to be almost uniform over the sample. At  $T$  range below  $\sim 150$  K, however,  $^{75}T_1$  exhibits an apparent distribution in association with the substitution of either Y or H. The short component  $^{75}T_{1S}$  and the long component  $^{75}T_{1L}$ , determined by the same method in ref. 16, are plotted in the figure. In  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$ , the  $^{75}(1/T_{1S}T)$  shows a nearly constant behavior above  $T_c$ , whereas  $^{75}(1/T_{1L}T)$  shows a gradual decrease upon cooling, which resembles the  $^{75}\text{As}$ -NMR result of  $\text{La1111(OPT)}$ .<sup>16</sup> It was reported that the  $^{75}(1/T_1T)$  at high  $T$  decreases markedly as the doping level of electron carriers increases in the  $\text{La1111}$

system,<sup>16,17</sup> which was corroborated by  $^{57}(1/T_1T)$ , as indicated in Fig. 3(b). Here, we note that the  $^{57,75}(1/T_1T)$  at 250 K for  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  is comparable to that for  $\text{La1111}(\text{OPT})$ . This reveals that the electron doping level of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  is close to that of  $\text{La1111}(\text{OPT})$ , confirming that the  $\text{Y}^{3+}$  substitution for  $\text{La}^{3+}$  does not change the doping level. By contrast, in  $\text{La1111H}$ , it is remarkable that the  $1/T_1T$ s of both  $^{57}\text{Fe}$ - and  $^{75}\text{As}$ -NMR at 250 K are markedly larger than those of  $\text{La1111}(\text{OPT})$ , the latter being comparable to  $^{75}(1/T_1T)$  for the underdoped  $\text{LaFeAsO}_{0.93}\text{F}_{0.07}$  ( $T_c = 22.5$  K).<sup>17</sup> This implies that  $\text{La1111H}$  is in an underdoped regime. When noted that the doped H atoms are located at the interstitial site surrounded by positively charged  $\text{Fe}^{2+}$  and  $\text{La}^{3+}$  sites (see Fig.2(a)), it is anticipated that the doped H atoms will exist as  $\text{H}^-$  ions to reduce the doping level. Furthermore, the significant increase in  $1/T_1T$  upon cooling was not observed in both compounds even though the Knight shift for  $\text{La}_{1-x}\text{Y}_x\text{1111}$  is almost constant against  $T$ ,<sup>10</sup> suggesting that strong AFM spin fluctuations do not develop in these compounds.

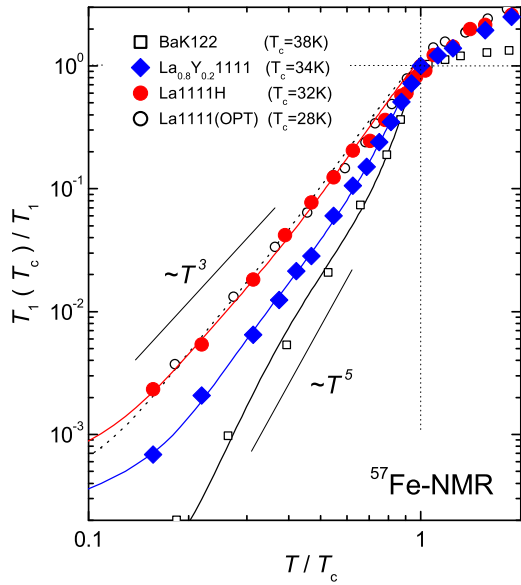


Fig. 4. (color online)  $T$  dependences of  $^{57}\text{Fe}-(T_1(T_c)/T_1)$  normalized at  $T_c$  in the SC state of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$ , along with the results reported for  $\text{BaK122}$  and  $\text{La1111}(\text{OPT})$ .<sup>18</sup> The multiple fully gapped  $s_{\pm}$ -wave model allows us to deduce the parameters for all the compounds listed in Table I through the fitting of the  $T$  dependence of  $^{57}\text{Fe}-(T_1(T_c)/T_1)$ . Here, the  $T_{1L}$  components are plotted for  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$ , since both  $T_1$ -components show the same  $T$  dependence when normalized by the values at  $T_c$ .

Next, we address the SC characteristics of these compounds. Figure 4 shows the  $T$  dependence of  $^{57}(T_1(T_c)/T_1)$  normalized at their  $T_c$ s. Since the  $T$  dependences of both  $T_{1S}$  and  $T_{1L}$  are almost the same,  $^{57}(T_{1L}(T_c)/T_{1L})$  is presented in the figure. The  $^{57}(T_{1L}(T_c)/T_{1L})$  of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  decreases similarly to  $\sim T^4$  upon cooling below  $T_c$ , which differs from either the  $\sim T^3$  in  $\text{La1111}(\text{OPT})$ <sup>15</sup> or the  $\sim T^5$  in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2(\text{BaK122})$ .<sup>18</sup> This emphasizes that a

common power law like the  $T$  dependence of  $1/T_1$  is not evident among Fe-based superconductors. These results are in contrast to the behavior of  $1/T_1 \sim T^3$  commonly observed in high- $T_c$  cuprates, which are  $d$ -wave superconductors with line-node gaps. Meanwhile, it was shown in the literature that the relaxation behaviors of both the  $\sim T^3$  in  $\text{La1111}(\text{OPT})$ <sup>15,19</sup> and the  $\sim T^5$  in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$  ( $\text{BaK122}$ )<sup>18</sup> are consistently reproduced in terms of the multiple fully gapped  $s_{\pm}$ -wave model.<sup>19</sup> This model is also applicable for understanding the SC characteristics of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  and  $\text{La1111H}$  as follows. According to Model B in the literature,<sup>18</sup> we assume that respective Fermi surfaces (FS1 and FS2) have isotropic gaps as  $\Delta^{FS1} \equiv \Delta_L$  and  $\Delta^{FS2} \equiv \Delta_S$ , and the fraction of the density of states (DOS) at FS1 is taken as  $N_{FS1}/(N_{FS1} + N_{FS2}) (=0.7)$ .<sup>20</sup> Furthermore, the coherence factor is neglected on the assumption that the interband scattering between the sign reversal gaps becomes dominant for the relaxation process in these compounds. In fact, the  $T$  dependence of  $^{57}(T_1(T_c)/T_1)$  of  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  is consistently reproduced with the parameters  $2\Delta_L/k_B T_c = 6.9$  ( $\Delta_S/\Delta_L = 0.35$ ) and the smearing factor  $\eta = 0.04\Delta_L$ ,<sup>20</sup> as is shown by the solid line in Fig. 4. A damping effect of quasiparticles due to impurity scattering introduced by the Y substitution can be deduced from  $\eta$ , which was actually larger than  $\eta_0$  in  $\text{La1111}(\text{OPT})$  (see Table I). Notably,  $2\Delta_L/k_B T_c = 6.9$  in  $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$  is larger than the  $2\Delta_L/k_B T_c = 4.4$  in  $\text{La1111}(\text{OPT})$ , revealing that the Y substitution into  $\text{La1111}$  increases  $T_c$  up to 34 K in association with a strong-coupling effect to mediate the Cooper pairs. Note that the strong-coupling effect enhances  $T_c$  despite the disorder introduced by Y substitution.

Table I. Evolutions of the SC gap ( $\Delta_L$ ) and smearing factor ( $\eta$ ) obtained from the analyses of  $^{57}\text{Fe}-(T_1(T_c)/T_1)$  assuming the multiple fully gapped  $s_{\pm}$  wave model (Model B) that was applied to  $\text{BaK122}$  and  $\text{La1111}(\text{OPT})$ <sup>18</sup> (see text). Here,  $\Delta_L$  represents the larger of the two full gaps.  $\eta/\eta_0$  represents a damping effect of quasiparticles additionally introduced by Y or H substitution, where  $\eta_0$  is defined as that of  $\text{La1111}(\text{OPT})$ .

|  | $T_c$<br>(K) | $a$<br>(Å) | $\alpha(^{\circ})^{\dagger}$ | $2\Delta_L/k_B T_c$ | $\eta/\Delta_L$ | $\eta/\eta_0$ |
|--|--------------|------------|------------------------------|---------------------|-----------------|---------------|
| $\text{BaK122}^{18}$                       | 38           | 3.914      | 109.7 <sup>21</sup>          | 9.4                 | 0.015           | 0.64          |
| $\text{La}_{0.8}\text{Y}_{0.2}\text{1111}$ | 34           | 4.004      | 112.3                        | 6.9                 | 0.04            | 1.3           |
| $\text{La1111H}$                           | 32           | 3.989      | 111.7                        | $\sim 4.7$          | $\sim 0.06$     | $\sim 1.3$    |
| $\text{La1111}(\text{OPT})^{18}$           | 28           | 4.023      | 113.2                        | 4.4                 | 0.05            | 1             |

<sup>†</sup>) The angle  $\alpha$  of As-Fe-As bonding is evaluated from the  $a$ -axis length at room  $T$  and a fixed bond length of Fe-As  $\sim 2.41\text{Å}$ , which holds empirically in  $\text{La1111}$  system.<sup>5</sup>

As for  $\text{La1111H}$ , it is possible that  $^{57}(T_{1L}(T_c)/T_{1L})$  is also reproduced roughly in terms of Model B with the parameters  $2\Delta_L/k_B T_c \sim 4.7$  ( $\Delta_S/\Delta_L = 0.35$ ) and  $\eta \sim 0.06\Delta_L$ , similarly to those in  $\text{La1111}(\text{OPT})$ , as shown by the solid line in Fig. 4. Despite the fact that the electron carrier density is lower than that in  $\text{La1111}(\text{OPT})$  and the disorder is heavily introduced into the Fe site, which is deduced from  $\eta/\eta_0 \sim 1.3$ ,  $T_c$  is enhanced up to 32 K. As a result, the reason why  $T_c$  increases in  $\text{La1111H}$  may

be closely related to the slight increase in the SC gap as well.

All the parameters listed in Table I are obtained from the analyses of the  $T_1$  results based on the two fully gapped  $s_{\pm}$  wave model (Model B). In the case of BaK122, which has the largest gap of  $2\Delta_L/k_B T_c = 9.4$ , the development of AFM spin fluctuations is argued to be the origin of the strong-coupling effect, making the SC gap quite large.<sup>18</sup> By contrast, the  $T_1$  measurements in the normal state do not point to the development of AFM spin fluctuations in La<sub>0.8</sub>Y<sub>0.2</sub>1111 or other La1111 systems.<sup>16</sup> The reason why  $2\Delta_L/k_B T_c = 6.9$  is larger in La<sub>0.8</sub>Y<sub>0.2</sub>1111 than in La1111(OPT) is not primarily ascribed to AFM spin fluctuations at low energies. We suggest that the structural parameter  $\alpha=109.7^\circ$  for BaK122<sup>21</sup> is the same as that of the regular tetrahedron, whereas the  $\alpha=112.3^\circ$  for La<sub>0.8</sub>Y<sub>0.2</sub>1111 is larger. This suggests that the SC energy gap increases as  $\alpha$  approaches  $\alpha=109.47^\circ$  for a regular tetrahedron. Furthermore, note that  $T_c$  increases as the  $a$ -axis length decreases in going from La1111(OPT) to BaK122, as shown in Table I. Here, we should comment on why the  $T_c$  in La1111H is lower than that in La<sub>0.8</sub>Y<sub>0.2</sub>1111, despite the structural parameters such as the  $a$ -axis length and the angle  $\alpha$  being closer to those of BK122 than to those of La<sub>0.8</sub>Y<sub>0.2</sub>1111; This may be because the electron doping level in La1111H is lower than that in La<sub>0.8</sub>Y<sub>0.2</sub>1111, in addition to some disorder effect. In this context, the optimization of both the structural parameters and the carrier doping level to fill up the bands is crucial for increasing their  $T_c$  through the optimization of the Fermi surface topology.

In summary, the systematic NMR measurements of La<sub>0.8</sub>Y<sub>0.2</sub>FeAsO<sub>1-y</sub> ( $T_c=34$  K) and LaFeAsO<sub>1-y</sub>H<sub>x</sub> ( $T_c=32$  K) have revealed that the Y<sup>3+</sup> substitution does not change the doping level in La<sub>0.8</sub>Y<sub>0.2</sub>1111, whereas H-doping decreases the carrier density in La1111H. The  $1/T_1$  results in the SC state for both compounds are consistently interpreted in terms of the multiple fully gapped  $s_{\pm}$ -wave model. Thus, it is highlighted that the SC gap and  $T_c$  in La<sub>0.8</sub>Y<sub>0.2</sub>1111 become larger than those in La1111(OPT) without any change in doping level. Furthermore, the  $T_c$  and SC gap in La1111H slightly increases even though the decrease in carrier density and some disorders are heavily introduced. We suggest that the primary reason why  $T_c$  is increased in these La-based 1111 compounds is neither the change in doping level nor the development of AFM spin fluctuations, but the structural parameters approaching their optimum values to increase  $T_c$  for the bond angle  $\alpha$  of the FeAs<sub>4</sub> tetrahedron and the  $a$ -axis length. Systematic spectroscopies of the SC properties of Ln1111 systems with the highest  $T_c$  of more than 50 K are highly desired in the future in order to clarify the Fermi surface topology, the antiferromagnetic spin fluctuations in the normal state, and their relevance to SC gap structures.

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- 1) Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono: J. Am. Chem. Soc. **130** (2008) 3296.
- 2) Z. A. Ren, W. Lu, J. Yang, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao: Chin. Phys. Lett. **25** (2008) 2215.
- 3) H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. **77** (2008) 063707.
- 4) Z. A. Ren, G. C. Che, X. L. Dong, J. Yang, W. Lu, W. Yi, X. L. Shen, Z. C. Li, L. L. Sun, F. Zhou, and Z. X. Zhao: Europhys. Lett. **83** (2008) 17002.
- 5) C. H. Lee, H. Eisaki, H. Kito, M. T. Fernandez-Diaz, T. Ito, K. Kihou, H. Matsushita, M. Braden, and K. Yamada: J. Phys. Soc. Jpn. **77** (2008) 083704.
- 6) P. M. Shirage, K. Miyazawa, H. Kito, H. Eisaki, and A. Iyo: Phys. Rev. B **78** (2008) 172503.
- 7) K. Miyazawa, K. Kihou, P. M. Shirage, C.-H. Lee, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. **78** (2009) 034712.
- 8) Y. Mizuguchi, Y. Hara, K. Deguchi, S. Tsuda, T. Yamaguchi, K. Takeda, H. Kotegawa, H. Tou, and Y. Takano: Supercond. Sci. Technol. **23** (2010) 054013.
- 9) K. Ishida, Y. Nakai, and H. Hosono: J. Phys. Soc. Jpn. **78** (2009) 062001.
- 10) H. Yamashita, M. Yashima, H. Mukuda, Y. Kitaoka, P. M. Shirage, and A. Iyo: Physica C (2009), doi:10.1016/j.physc.2009.11.125.
- 11) P. Jeglič, J.-W. G. Bos, A. Zorko, M. Brunelli, K. Koch, H. Rosner, S. Margadonna, and D. Arčon: Phys. Rev. B **79** (2009) 094515.
- 12) M. Tropeano, C. Fanciulli, F. Canepa, M. R. Cimberle, C. Ferdeghini, G. Lamura, A. Martinelli, M. Putti, M. Vignolo, and A. Palenzona: Phys. Rev. B **79** (2009) 174523.
- 13) K. Miyazawa, S. Ishida, K. Kihou, P. M. Shirage, M. Nakajima, C. H. Lee, H. Kito, Y. Tomioka, T. Ito, H. Eisaki, H. Yamashita, H. Mukuda, K. Tokiwa, S. Uchida, and A. Iyo: Appl. Phys. Lett. **96** (2010) 072514.
- 14) H. Mukuda, N. Terasaki, H. Kinouchi, M. Yashima, Y. Kitaoka, S. Suzuki, S. Miyasaka, S. Tajima, K. Miyazawa, P. M. Shirage, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. **77** (2008) 093704.
- 15) N. Terasaki, H. Mukuda, M. Yashima, Y. Kitaoka, K. Miyazawa, P. M. Shirage, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. **78** (2009) 013701.
- 16) H. Mukuda, N. Terasaki, N. Tamura, H. Kinouchi, M. Yashima, Y. Kitaoka, K. Miyazawa, P. M. Shirage, S. Suzuki, S. Miyasaka, S. Tajima, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. **78** (2009) 084717.
- 17) Y. Nakai, S. Kitagawa, K. Ishida, Y. Kamihara, M. Hirano, and H. Hosono: New J. Phys. **11** (2009) 045004.
- 18) M. Yashima, H. Nishimura, H. Mukuda, Y. Kitaoka, K. Miyazawa, P. M. Shirage, K. Kiho, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. **78** (2009) 103702.
- 19) Y. Nagai, N. Hayashi, N. Nakai, H. Nakamura, M. Okumura, and M. Machida: New J. Phys. **10** (2008) 103026.
- 20) We note that both Models A and B in the literature<sup>18</sup> can reproduce the present results with similar parameters, although only the results based on Model B are shown.
- 21) M. Rotter, M. Tegel, and D. Johrendt: Phys. Rev. Lett. **101** (2008) 107006.